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(54) Title: SUPPRESSION OF FINES FORMING IN A FLUIDIZED BED ETHYLENE POLYMERIZATION PROCESS

(57) Abstract

Disclosed is a method for controlling or reducing the amount of powder fines present in a polyethylene fluidized bed reactor. The method uses hydrocarbons that are inert with respect to the polymerization reaction, as well as using reactive olefins. The reduction of powder fines provides significant operating benefits in the fluid bed process, including reduced formation of powder agglomerates in the reactor and reduced fouling of equipment in the recycle gas stream.

SUPPRESSION OF FINES FORMING IN A FLUIDIZED BED ETHYLENE POLYMERIZATION PROCESS

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This is an ORIGINAL application based on the PROVISIONAL Serial No. 60/005,374 filed October 16, 1995.

10   FIELD OF THE INVENTION
The present invention relates to a process for the reduction or suppression of powder fines in a fluid bed polyethylene process. More particularly, the present invention relates to a process for the reduction or
15   control of fines to a low level in a polyethylene production process of a fluid bed reactor through the introduction of additional hydrocarbons.

                          BACKGROUND OF THE INVENTION
20   It is well known that many polymers can be produced as powders in fluid bed reactors wherein the fluidization is provided by a circulating mixture of gases that includes the monomers. This technology is widely used commercially for polyolefins and polyolefin
25   copolymers. One particularly useful arrangement of a fluid bed polyolefin process is disclosed in U. S. Patent No. 4,882,400. Other examples of fluid bed polyolefin technology are demonstrated in the references that follow.
30   The active, growing powder in a fluidized bed polyolefin reactor is composed of a wide range of particle sizes. Thus, this powder is referred to as having a broad particle size distribution. Some of the reasons for this broad size distribution are the size
35   range of the initial catalyst particles (or prepolymer particles) charged to the reactor, the difference in catalytic activity of each catalyst particle, the

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difference in residence time for each growing polymer
particle, the agglomeration of polymer particles, and
the spalling of polymer particles.

The size distribution of particles can be
characterized by various physical measurements relating
to the particle mass, physical dimensions, or specific
surface area. Two commonly used methods of measurement,
owing to ease and reproducibility, are mechanical sieve
analysis and the light scattering behavior of a cloud of
particles. The very small polymer particles are called
fines. As used in the art, the term "fines" refers to
some defined fraction of the polymer powder particles
that are smaller than the average of the entire
population of powder particles present in the fluid bed.
Particularly small polymer particles, for example,
smaller than 125 microns are considered fines.

In the fluid bed processes for the production of
polyethylene and ethylene copolymers, high levels of
polymer powder fines in the reactor pose significant and
well known operating difficulties. Within the reactor,
a higher level of fines often leads to increased
agglomeration of the polymer powder. Outside the
reactor, the fines may deposit in the recycle system and
grow, fouling the piping, heat exchangers, compressors,
and the reactor inlet gas distribution grid.

Inside the reactor, fines are a leading contributor
to the formation of powder agglomerates. For various
reasons, fines tend to segregate into certain poorly
circulated and poorly cooled regions of the reactor.
Exacerbating the segregation problem is the tendency of
fines to have higher than average catalytic activity,
thus tending to be hotter than the average particle.
This higher catalytic activity in fines is due to higher
concentrations of active catalyst components in the

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fines and due to short diffusion paths for monomers and
for co-catalyst molecules.

One undesirable place at which fines accumulate is
along the reactor vessel wall in the zone occupied by
the main fluid bed. This accumulation is believed to
occur because fines are more greatly affected by static
forces due to their larger ratio of surface area (static
charge) to mass (inertia). Thus, fines can cling by
static electric forces to the electrically grounded
metal wall of the reactor. Polymerization in the
stagnant layer of reactor wall fines releases heat which
can lead to melting and fusing of polymer into sheets
along the vessel wall. These sheets of fused polymer
may grow quite large before coming loose and falling
into the fluid bed. Once fallen into the main fluid
bed, such sheets can obstruct powder fluidization,
circulation, and withdrawal. In some cases, the sheets
may be so large as to significantly disrupt the normal
fluidization and circulation of gas and solids of the
entire fluid bed leading to extensive fusing of the main
bed. When powder withdrawal slows or the bed fuses, the
reactor production must be stopped and the reactor
vessel opened for cleaning. This is a very costly
production outage.

Another undesirable place where fines accumulate is
in the disengaging section of the reaction vessel. The
disengaging section of the reactor is a region of
expanded cross-sectional area that is above the zone in
which bed level normally resides. The purpose of the
expanded area is to reduce the velocity of the
fluidizing gas in order to minimize the entrainment of
fine particles in the gas leaving the reactor. In the
disengaging section, fines tend to concentrate in the
regions of lower gas velocity nearer the downward

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sloping vessel wall. In fact, it is intended that most
of the fines fall onto the sloped wall of the
disengaging section and slide downwards and back into
the main fluidized bed. However, when the concentration
of fines increases in the disengaging section, the
polymerization heat load on the sloped wall becomes
larger. This can be observed by increasing temperatures
seen from indicators placed in the sloped wall in the
disengaging section. The concentration of fines and
resulting heat can become great enough to lead to
melting and fusing of the powder into sheets along the
sloped wall. These sheets will tend to grow until their
own weight and hydrodynamic forces cause them to fall
into the main fluid bed, there, as discussed above,
obstructing powder withdrawals and possibly causing more
extensive bed fusing. As with the above, when either of
these occur, the reactor production must be stopped and
the reactor vessel opened for cleaning.

Several technologies are known for modification of
static and of wall sheeting behavior. These include
U.S. Pat. No. 4,803,251 demonstrating the addition of
different compounds to the fluid bed reactor to adjust
static voltage; U.S. Pat. No. 4,532,311 disclosing the
use of chemicals to reduce the bonding of sheets to the
reactor vessel wall; European Patent Application
0,453,116,A1 disclosing the addition of known antistatic
agents to a fluid bed polyolefin reactor; European
Patent Application 0,604,990,A1 disclosing the use of an
electrode near the grid; and U.S. Pat. No. 5,461,123
disclosing the use of sound waves to dislodge fines from
the reactor wall.

A particularly relevant discussion of the operating
problems brought on by the presence of fines in the
disengaging section of the reactor is contained in U.S.

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Pat. No. 5,428,118. This patent discloses the modification of the circulating pattern of fines in the disengaging section in order to reduce operating and product quality problems.

In addition to problems caused inside the reactor, problems are also caused by fines outside the fluid bed reactor vessel. Some fines will leave the reactor vessel in the overhead piping that carries the recycle gas away for cooling and compression. The exiting fines may attach to surfaces of piping, heat exchangers, and other process equipment in the recycle loop. Recycled fines may also settle in regions of lower gas velocity, such as the bottom of the reactor underneath the distribution grid for the fluidizing gas.

Because fines exiting the reactor retain their catalytic activity, they continue to react outside the reactor. Thus, fines depositing in the recycle system equipment grow and fuse to create skins, sheets, and lumps of polymer. These skins, sheets, and lumps reduce heat transfer efficiency and modify mass flow in the recycle gas piping and equipment. Also, some fines will return to the reactor via the recycle system. Because the temperature and gas composition are very different at some locations in the recycle system, the polymer produced outside the reactor may have very undesirable properties. Although a minute fraction of the total polymer production, the fines returning to the reactor can nonetheless seriously impact the suitability of the overall product. The presence of non-homogeneous polymer fines in the final product can significantly affect the quality of the product and resulting articles produced therefrom, such as the formation of gels in polyethylene films.

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There are several disclosed methods for coping with reactive fines exiting a fluidized bed reactor. U. S. Pat. No. 4,882,400 discloses the use of cyclonic separators to remove the fines from gas exiting the reactor and the use of ejectors to return the fines to the reactor. U. S. Pat. No. 4,956,427 discloses technology for coating the surface of heat exchanger tubes to reduce the adhesion of fines and the formation of insulating polymer skins. U. S. Pat. No. 5,126,414; U. S. Pat. No. 4,933,149; and U. S. Pat. No. 5,352,749 all reveal improvements to mitigate problems with the accumulation of fines and lumps underneath the gas distribution grid in the reactor.

The above patents disclose methods of coping with the problems caused by polymeric fines only after they are produced. These references disclose various methods of preventing sheeting, through either physical, electrostatic, or chemical means of controlling the behavior of the fines. However, none of the above references discloses a method of preventing or reducing the production of fines. None of these references deal with the original problem of the formation of the fines during polymerization.

However, techniques for the modification of catalysts have been used for controlling the level of fines in the fluid bed. The size of the catalyst support, the size of the finished catalyst, the physical strength of the support and the chemical activities of the catalyst system are some of the catalyst parameters known to affect the particle size distribution in a fluid bed polyolefin reactor. Examples are given by P. Galli in "The 'Spherilene' Process", paper S4A, Polyethylene – The 1990s and Beyond, The Plastics and Rubber Institute (UK), (1992) and by I.D. Burdett in "A

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Continuing Success: The UNIPOL Process", P 616—623,
CHEMTECH, October 1992. Unfortunately, when the
catalyst is altered, then the process parameters and
polymer properties are also altered. Catalyst changes
5   often result in a modified polymer, such as changes in
the density and molecular weight distribution.

In light of the above, it would be very desirable
to be able to control to a low level or to reduce the
amount of fines produced in the reactor, thereby
10   avoiding the necessity of dealing with the problems
caused by the fines, but without having to modify the
catalyst, thereby avoiding changes to the properties of
the resulting polyethylene polymer.

15   SUMMARY OF THE INVENTION
The process according to the present invention
entails a method for reducing or controlling the fines
to a low level in a fluid bed polyethylene process which
comprises: determining the fraction of polymeric fines
20   present in the fluid bed reactor and adjusting the
chemical composition of the fluidizing gas mixture; if
the fraction of fines in the fluid bed of the reactor is
too high, then an amount of an inert $C_3 - C_8$ hydrocarbon
is added to the fluidizing gas mixture; if the fraction
25   of the fines is reduced below the target fraction of
fines, then the amount of inert $C_3 - C_8$ hydrocarbon
added to the fluid bed reactor can be lowered.

Another process of controlling or reducing the
fines to a low level according to the present invention
30   in a polyethylene fluid bed reactor comprises measuring
the amount of fines and the composition of the gas
mixture in the reactor and then determining the ratio of
the total reactor pressure to the dewpoint pressure of
the reactor gas; if the fines level is too high and the

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ratio of Ptotal/Pdew is below 0.4, then an amount of
inert $C_3 - C_8$ hydrocarbon is added to the reactor to
increase said ratio to at least 0.4 or above.

The overall polymerization process according to the
present invention entails a process for the production
of polyethylene with a controlled or reduced fraction of
powder fines that comprises (1) introducing into a
fluidized bed of a gas phase reactor at least one alpha-
olefin, hydrogen, other fluidizing gas, catalyst, and
inert $C_3 - C_8$ hydrocarbon and determining the ratio of
the total reactor pressure to the dewpoint pressure of
the reactor gas such that if the ratio is below 0.4,
inert $C_3 - C_8$ hydrocarbon is introduced into the
reactor, and if the ratio is above 0.99, reducing the
amount of inert $C_3 - C_8$ hydrocarbon introduced into the
reactor; (2) removing a portion of the alpha-olefin,
hydrogen, other fluidizing gas, inert $C_3 - C_8$
hydrocarbon, and polyethylene produced therein; and (3)
reintroducing fluidizing gas, inert $C_3 - C_8$ hydrocarbon,
alpha-olefin, and hydrogen.

Another process according to the present invention
entails the control or reduction of fines to a low level
in a polymerization reactor in a fluid bed polyethylene
process which comprises: determining the fraction of
polymeric fines present in the fluid bed reactor and
adjusting the composition of the reactive chemicals in
the fluidizing gas mixture; if the fraction of fines in
the fluid bed of the reactor is too high then increasing
the amount of the blend of ethylene/comonomer/hydrogen
introduced into the reactor to reduce the production of
fines, without significantly modifying the density or
molecular weight of the polymer.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows one useful arrangement of a fluid bed polyolefin process.

Fig. 2 shows the absorption of hexene-1 into particles
5   of a linear low-density polyethylene (LLDPE), an
ethylene/hexene copolymer sample, at two temperatures
and at various concentrations of hexene-1 gas around the
polymer.

Fig. 3 shows the response of the amount of fines
10   fraction in an operating reactor while raising and
lowering the amount of inert C_6 hydrocarbons in the
fluidizing gas with all other conditions remaining
essentially constant.

Fig. 4 shows the response of the median particle size
15   during the same period of reactor operation as Fig. 3

Fig. 5 shows that there was not any condensed liquid in
the reactor inlet gas during the same time period shown
in Figs. 3 and 4.

Fig. 6 shows the response of the average fines fraction
20   of an operating reactor on nine successive production
periods of a particular density of LLDPE when the levels
of inert C_6 hydrocarbons were intentionally raised.

DETAILED DESCRIPTION OF THE INVENTION

25   The inventors have unexpectedly discovered a
particularly useful and surprising method for
controlling or reducing the amount of fines within a
fluid bed reactor during production of polyethylene and
ethylene copolymers. The inventors have unexpectedly
30   found that by controlling the hydrocarbon composition of
the fluidizing gas inside the reactor, a significant
measure of control over the level of fines present in
the reactor is achieved. Specifically, inert
hydrocarbons are added to the circulating gas for the

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purpose of controlling or reducing the level of fines in
the fluid bed. The invention has the advantages of
permitting higher production rates without the formation
of agglomerates in the reactor and of reducing the
5   fouling of recycle stream piping and heat exchangers.
        The reduction or control in reactor bed fines is
obtained without significantly modifying the properties
of the polymer produced. The present process permits
this reduction in the amount of fines produced without
10   the need to modify the catalyst system, either
chemically or physically.
        The quantitative reduction of fines achieved by the
current invention varies depending on the target product
grade being made in the reactor. However, the reduction
15   of fines is frequently on the order of 50 percent,
compared to operation with lower levels of inert
hydrocarbons. In some cases, the reduction in the
production of fines may even be greater than 50 percent.
        Procedures are revealed herein for using the inert
20   hydrocarbons singly or in combination and at differing
reactor temperatures and pressures. This is an
important feature of the present invention because
different inert hydrocarbons can provide different
levels of fines suppression and the effect can vary for
25   any particular hydrocarbon according to the reactor
temperature and pressure.
        The process according to the present invention of
the lowering of fines is achieved without modifying
significantly the product properties. Surprisingly, the
30   inventors have found that the level of fines can be
suppressed using inert hydrocarbons in the $C_3 - C_8$
range that do not significantly modify the properties of
the target product being made in the reactor.
Furthermore in contrast to the previously known

processes, the current invention modifies the level of
fines in the reactor, by a method not previously
contemplated, without modification to the catalyst
system. In many respects, control of fines without
5   modification of the catalyst system is superior because
it is difficult to change the catalyst system without
affecting the properties of the polyolefin produced, and
the current invention reduces the amount of fines
without measurably changing product properties.

10   The inventors have also discovered that the
lowering of fines occurs without regard to whether or
not liquids are condensed in the fluidizing gas recycle
stream. The higher levels of inert hydrocarbons change
the heat capacity and dewpoint of the fluidizing gas.

15   Depending on reactor heat load and the flow of
fluidizing gas, some liquids may be produced during
cooling of the recycle stream, and various methods are
known for returning these liquids to the reactor.
However, the inventors have discovered that the

20   suppression of fines using inert hydrocarbons works
similarly both with and without the addition of liquids
to the fluid bed.

In contrast to technologies that seek to cope with
the existence of fines in a fluid bed polyolefin

25   reactor, the current invention controls or reduces the
quantity of fines to a low level in the fluid bed and in
the recycle stream by a method not previously
contemplated. In many respects, the actual reduction of
fines is a superior method for avoiding operating

30   problems. The current invention speaks to the root
cause of a problem rather than providing a method that
merely compensates for an elevated level of fines.

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Without being bound to any particular theory for
the function and efficacy of the invention, the
inventors believe that absorption of the hydrocarbons
into the growing polymer powder may be an operative

5   physical phenomena that permits the reduction in the
production of fines during polymerization.

Ethylene copolymers can absorb considerable amounts
of hydrocarbon. This absorption is observed to be a
function, primarily, of the density of the polymer and

10   of the concentration of the hydrocarbon in the vapor
phase around the polymer. At low levels of vapor
concentration, absorption of hydrocarbon tends to be a
linear function of vapor concentration. At higher
levels of vapor concentration, the absorption typically

15   becomes quite non—linear as shown in Fig. 2 and
explained in Example 1. For example, a linear low
density polyethylene (LLDPE) with a density of about
0.920 gram per cubic centimeter may absorb upwards of 20
percent of its own weight when placed in contact with a

20   liquid hydrocarbon. This behavior is widely reported in
the open literature; one thorough review is given by
R.A. Hutchinson and W.H. Ray in "Polymerization of
Olefins through Heterogeneous Catalysis. VIII. Monomer
Sorption Effects", Journal of Applied Polymer Science,

25   Vol. 41, 51—81 (1990).

Absorption of hydrocarbon into the polyethylene is
observed to modify the polymer physically by swelling
and plasticizing it. At an elementary level, this may
be studied by feel, sight and even sound when as little

30   as 4 weight percent C_6 is absorbed into a powder sample
in a glass jar at room temperature and pressure. Again,
without wishing to be bound to a specific theory, the
inventors suggest that plasticizing of the polymer
powder may perhaps be a fundamental behavior behind the

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benefits of the current invention. Plasticization may make the powder more resistant to breakage, or it may even permit some particles to re—agglomerate.

Absorption of hydrocarbon may also buffer temperature swings in the growing particles. Although fluid bed polymer processes have a high degree of temperature uniformity within the powder bed, nonetheless there are regions of unequal temperature in the reactor, notably near the recycle stream inlets, along the vessel walls, and in the disengaging section above the main fluid bed. Additionally, there are thermal gradients within individual particles when they are actively producing new polymer.

The equilibrium absorption of hydrocarbons into ethylene copolymers decreases with increasing temperature, and the desorption process involves a latent heat that is similar to the cooling produced by simple evaporation. Thus, when particles tarry in a hot region of the reactor and begin to overheat, some hydrocarbon will desorb from the powder causing a cooling effect. Conversely, when particles circulate into the cool zone above the recycle gas inlet grid, there will be a rise in hydrocarbon absorption, producing a latent heat of absorption that will serve somewhat to counteract the cooling of the recycle stream. Again without wishing to be bound by theory, it is possible that increased levels of absorption provide increased thermal buffering to mitigate temperature swings within individual particles. This will, in turn, dampen thermally driven activity swings and thermally induced stresses in the particles, perhaps reducing their tendency to fracture and form fines.

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The absorption interpretation has allowed the
inventors to develop a more sophisticated approach for
setting the level of inert hydrocarbon used to reduce
fines. This method takes into account different reactor
5   temperatures, pressures, and more widely varying gas
phase compositions. Absorption in the polyethylene
depends upon the thermodynamic activity of the
surrounding hydrocarbon phase. For a pure component,
such as hexene–1 or n–hexane, this activity may be
10   approximated by the partial pressure Pi of the specific
hydrocarbon, divided by its vapor pressure at the
particular temperature, Pi*. As the temperature
changes, vapor pressure Pi* changes, higher temperature
giving higher vapor pressure and lower absorption as
15   shown in Fig. 2 and Example 1.

The effect of mixtures of different hydrocarbons
can be predicted by summing the individual Pi/Pi*, thus
calculating Σ(Pi/Pi*). The inventors have found that
useful reductions in fines can be obtained by raising
20   the total hydrocarbon level to ensure that the Σ(Pi/Pi*)
for all components in the reactor gas is above 0.4.

In Example 2 below, the inventors initially used a
simple method for monitoring the amount of C_6
hydrocarbon in a reactor. The partial pressure is
25   summed for all C_6 compounds, including both alpha–olefin
and inert compounds, in the reactor gas phase. As this
summed partial pressure is raised, the increasingly
higher levels of hydrocarbons tend to give even lower
concentrations of fines. The summed partial pressure of
30   heavier hydrocarbons is the simplest method for
predicting the onset and magnitude of fines reduction.

A preferred embodiment of the present invention is
to add intentionally to the reactor gas phase
hydrocarbons in the C_3 to C_8 range, which are inert with

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respect to the polymerization, to increase (Pi/Pi*) at least above 0.4, and preferably as high as possible subject to other process constraints, thereby improving process operation with respect to agglomeration and fouling from the reactive powder fines of polyethylene and ethylene copolymers.

As the sum of the Pi/Pi* increases above 0.4 up to near 1, the amount of hydrocarbon absorbed in the polymer continuously increases. When the polymer product is removed from the reactor, the absorbed hydrocarbon must be removed and recycled. Thus, the higher the Pi/Pi* the more hydrocarbon there is that must be desorbed and recovered. This absorbed hydrocarbon also can interfere with the powder flowability and powder fluidization. Therefore, if the control or reduction of fines is adequate, the amount of hydrocarbon added to the system should not be arbitrarily increased further.

A more accurate prediction for absorption into polyethylene from complex mixtures of reactor gas can be obtained by finding the ratio of the reactor pressure to the dewpoint pressure for the gas composition and temperature in the reactor. Changing the amount of C_3 to C_8 inert hydrocarbons will change the dewpoint pressure. Higher loading of heavy hydrocarbons will reduce the dewpoint pressure and will cause Ptotal/Pdew to rise. The inventors have unexpectedly found that useful reductions in fines can be obtained when Ptotal/Pdew in the reactor is raised above 0.4. This Ptotal/Pdew should not rise to be equal to one or greater, because this means that liquid would be present in the reactor overhead gas flow. This is undesirable because then the reactor commences to fill with liquid. This ratio of Ptotal/Pdew is preferably monitored and

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maintained between 0.4 and 0.99, more preferably between
0.5 and 0.95 with a ratio between 0.6 and 0.9 being most
preferred.

    The inert hydrocarbon used in the process according
5   to the present invention can be any hydrocarbon that is
inert under the polymerization reaction conditions, and
can also include non—alpha—olefins, such as hexene—2, if
they are inert with the catalyst system in use. The
inert hydrocarbons are C_3-C_8 hydrocarbons, preferably C_4
10   to C_6 with the C_5-C_6 hydrocarbons being most preferred.
Suitable examples of saturated, inert hydrocarbons
include n—butane, isobutane, 2,2—dimethyl propane,
isopentane, n—pentane, n—hexane, cyclohexane,
2—methylpentane, 2,3—dimethylbutane, 2,2—dimethylbutane,
15   3—methylpentane, and methylcyclopentane. The C_5-C_6
inert hydrocarbons are more preferred, since these give
the best balance between volatility, allowable partial
pressure, and absorption.

    Because the invention works without modifying the
20   preparation or strength of the catalyst, including any
inorganic support structure such as $MgCl_2$ or silica, and
because the invention works without altering the product
properties set by the catalyst system, the invention is
not dependent on the specific type of catalyst system.
25   The level of benefit obtained may depend upon the base
level of fines inherent with the specific catalyst
system in use, but the general utility of the invention
results from the interaction of the hydrocarbons in the
gas phase with the polyethylene, not with the catalyst
30   used to produce it.

    The inventors have discovered that with a
particular catalyst system with an inherent base level
of fines, that as the density is decreased by increasing
the ratio of comonomer to ethylene, then the level of

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fines produced in the reactor also tends to decrease.
However, operating problems caused by fines depend upon
the particular polymer characteristics as well as their
amount. For example, a level of fines which permits
5   good operation at a polyethylene density of 0.952
gram/cc can produce severe behavior at a lower product
density of 0.930 gm/cc.

The inventors have discovered that the fines
produced in a fluid bed polyethylene reactor operating
10   in the density range of 0.94 to 0.91 gram/cc, though
reduced in quantity compared to higher densities,
produce significant operating difficulties. This may be
due to the fact that the polymer becomes softer and
stickier as the density is reduced. Whatever the cause,
15   the inventors have discovered that the present invention
is surprisingly and particularly useful when the
polyethylene product density is in the range of 0.94 to
0.91 gram/cc, with more particular benefits in the range
of 0.94 to 0.92 gram/cc and most improved results in the
20   range of 0.935 to 0.922 gram/cc.

In order to produce a lower density polyethylene
product, the ratio of comonomer to ethylene is
increased, often by keeping ethylene near constant and
increasing the fraction of comonomer in the reactor gas
25   phase. The presence of additional comonomer causes
increased incorporation of the heavier olefins in the
ethylene copolymer, and this lowers the density of the
product powder. As noted above, lower densities usually
exhibit lower levels of fines. Since the flexibility
30   and melting behavior of an ethylene copolymer change
when the density is lowered, the density may itself be
supposed to control the amount of fines present in the
fluid bed.

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However, the inventors have unexpectedly discovered that the comonomer in a fluid bed polyethylene process can be used, according to the present invention, to reduce the production of fines without altering to a significant extent the density of the polymer. This can be accomplished by increasing the total blend of monomer, e.g. ethylene and hexene, such that the density remains the same while increasing the P/P* or Ptotal/Pdew to be within the range required according to the present invention. This aspect of the present invention has it's limitations, and when the comonomer is butene-1, the reduction in fines may not be sufficient, or may be constrained by the amount of total ethylene present in the reactor. Thus, this aspect of the present invention is useful for C_3 to C_8 olefin comonomers, but the preferred embodiment is with C_5 to C_6 olefin comonomers.

As used herein, the term ethylene polymers, ethylene copolymers, or polyethylene also includes copolymers composed of ethylene and one or more other olefins (comonomer). These other olefins are preferably alpha-olefins. Also included in this definition of polymers are terpolymers of ethylene and two or more comonomers. Examples of suitable alpha-olefins include, but are not limited to, propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, and octene-1, with hexene-1, 4-methylpentene-1, and butene-1 being most preferred. These ethylene copolymers, are in most instances linear, and are referred to as linear low-density polyethylene (LLDPE) at densities below .94 g/cc.

As used herein, the term "fines" refers to some defined fraction of the powder particles that are smaller than the average of the entire population of

powder particles present in the fluid bed. There are
many convenient methods for measuring the size
distribution, and any of these can used to practice the
present invention. Similarly, the definition of how

5   large a particle remains a fines is somewhat arbitrary
though it would not typically be chosen to include more
than one-half, and preferably less than one-quarter, and
most preferably less than one-tenth of the total
particle population. The choice of measurement method

10   and size definition can be made for any number of simple
reasons, but it is generally based upon cost and
reproducibility.

Key elements in the reactor loop for a preferred
polyethylene process are illustrated in Fig. 1 and

15   include the reactor vessel 1, heat exchangers 2 and 4,
compressor 3, fines cyclone 6, and fines return injector
7. A gas distributor plate 8 is provided near the
bottom of the reactor. An enlarged disengaging zone 5 is
provided near the top of the vessel for reducing the

20   entrainment of solids in the exiting gas. Various
schemes are used for replenishing the ethylene,
comonomer, hydrogen, and inerts in the main gas recycle
system. These are depicted in Fig. 1 as a single
combined stream 9 for simplicity. Catalyst injection,

25   in the form of prepolymer, is shown by stream 10, and
polymer powder discharge is shown as stream 11.

Additionally, during start-up of the reactor, a
high amount of fines can be produced. The production of
this amount of fines can be reduced by adding inert

30   hydrocarbon according to the present invention.

The following examples are intended to illustrate
the present invention, and are not intended to be
interpret as a limitation upon the reasonable scope
thereof.

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EXAMPLES

As used in the art, the term "fines" refers to some
defined fraction of the powder particles that are
smaller than the average of the entire population of
powder particles present in the fluid bed. As an
arbitrary matter of convenience, the data presented in
the Examples herein consider fines to be the percentage
of particles smaller than 125 microns in diameter as
measured with a laser diffraction meter, Malvern Series
2600, available from Malvern Company. A different size
definition, of say 80 microns, or a different
measurement method, such as sieving, would serve equally
well to show the effects of the invention and to
correlate with the improved operation afforded by the
invention.

Example 1

This example illustrates absorption of hexene-1 in
a linear low-density polyethylene. The polyethylene
used was a copolymer of ethylene and hexene-1 with a
nominal melt index of 1 gram/10 minutes (ASTM Test
Method D1238 Condition E), and a nominal density of
0.920 gram per cubic centimeter. The polymer sample was
placed on a micro-gram balance inside a thermostated,
isothermal vacuum chamber, which was fully evacuated.
Then, various pressures of hexene-1 vapor were admitted
to the vapor space, and the weight change in the polymer
sample was noted. This weight change was corrected for
buoyancy in the vapor phase, and converted to a weight
percent absorbed in the polymer. The experiment was
performed at two different temperatures, 50°C and 70°C.
The results plotted in Fig. 2 show the weight percent
absorption on the Y-axis plotted against the ratio of
the partial pressure of the hexene-1 divided by the

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vapor pressure of the hexene—1 on the X—axis. This
ratio of partial pressure to vapor pressure may be
represented as P/ P*. It will be noted that the
absorption of hexene—1 into the polymer approaches 20%,
5   as the pressure of hexene—1 in the vapor phase
approaches the vapor pressure of liquid hexene at the
temperatures studied. When the ratio of P/P* reaches 1,
there would be liquid hexene—1 present. It will be
noted that dividing the partial pressure in the vapor
10   phase by the vapor pressure appears to normalize the
results from the two experiments at 50 and 70°C onto a
common response curve. This means that as the polymer
sample becomes hotter, the pressure of the hexene—1 in
the vapor phase must become much higher to produce an
15   equivalent absorption in the polymer. This
normalization using vapor pressure provides a useful
tool to estimate the absorption behavior of the
hydrocarbon at different temperatures not studied.

20   Example 2
       An experiment was conducted in a research scale
fluid bed reactor unit with a reactor diameter of about
29 inches (74 cm). The polymer produced was an ethylene
copolymer with hexene—1. The nominal density was
25   controlled at 0.924 gram per cubic centimeter throughout
the experiment by small adjustments in the ratio of
hexene—1 to ethylene. The nominal melt index was
controlled at 0.9 gram/10 minutes throughout the
experiment by small adjustments in the ratio of hydrogen
30   to ethylene. The reactor temperature was controlled
near 84°C and pressure was held near 290 Psig (2.00
MPa). Polymer production averaged about 160 pounds per
hour (73 kg/hr) with an average residence time of about
3.4 hours during the test. Reactor gas composition

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included about 24 mole percent ethylene and about 4.4
mole percent hydrogen. The partial pressure of hexene—1
was about 3.2 mole percent, 10 psia (0.069 MPa). The
summed partial pressure of all C_6 hydrocarbons is shown
5   in Fig. 3, 4, and 5. The inert C_6 hydrocarbon can be
found by subtracting the baseline of hexene—1. There
was a trace of ethane and the balance of the reactor gas
was mostly nitrogen. The other particulars of the fluid
bed process and the Ziegler catalyst are generally
10   according to Example 2 in U. S. Pat. No. 4,882,400,
which is incorporated here in its entirety by reference.

The injected hexane was a commercial grade composed
of approximately 86 mole percent n—hexane, 10 mole
percent methylcyclopentane, and 4 mole percent
15   3—methylpentane. The source of the hexane injected on
days 6 and 10 was from the hexane storage facility of an
operating fluid bed polyethylene unit. The source of
hexane for the third injection sequence commencing on
day 18 was directly from a supplier's truck shipment
20   before unloading the balance of the shipment to the
commercial polyethylene unit. The hexane for the third
trial was dried over 3A molecular sieves. The hexane
for the first two trials had been dried by distillation
in the commercial polyethylene unit.

25   The results show that addition of hexane reliably
and reproducibly suppresses the level of fines present
in the fluid bed beginning within two (2) turnovers of
the bed. The fines rapidly reduce to drop below 50
volume percent of the original fines after a hexane
30   partial pressure of about 6—8 psia is added to the
reactor (See Fig. 3). Furthermore, the level of fines
is seen to rise when addition of the hexane is stopped.
Supporting the reduction in fines is evidenced by an
increase in the particle size of the total powder, as

illustrated in Fig. 4. The median particle size in
microns was increased from 1,000 to over 1,100 after
hexane was added.

Before addition of the hexane, (Pi/Pi*)
5   approximately equals (10 psia/26.9 psia) = 0.37. With
the supplemental 6 psia of hexane, (Pi/Pi*)
approximately equals 0.37 plus (6 psia/23.1 psia) = 0.37
+ 0.26 = 0.63.

In spite of the elevated level of C6 in the gas
10   composition, resulting from injection of hexane, the
temperature of the cold gas returning to the base of the
reactor never dropped down below the dewpoint of the
mixture. That is, there was never any liquid condensed
in the recycle stream. Fig. 5 shows a brief excursion
15   down to a 6°C margin between the dewpoint and the
temperature of the cold gas returning to the reactor,
but the usual margin was over 10°C.

Example 3
20   This example is a calculation to illustrate how to
calculate the required amount of hexane addition to
achieve a similar fines reduction at two different
temperatures. For n—hexane at 80°C, the vapor pressure
is about 20.6 psia (0.142 MPa). At 86°C the vapor
25   pressure of n—hexane is about 24.5 psia (0.169 MPa). To
achieve similar fines reduction behavior, about 19
percent more n—hexane is estimated to be required in the
gas phase at 86°C than at 80°C.

30   Example 4
This example is a calculation to illustrate how to
estimate equivalent amounts of different inert
hydrocarbons. For 6 psia (0.041 MPa) of n—hexane at
84°C, Pi/Pi* equal to 6/23.1 = 0.26. For a similar

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reduction in fines, only slightly less hexene-2, which
is sterically hindered from reacting when using
conventional Ziegler catalysts, is needed. An
equivalent reduction is predicted with about 5.9 psia
5   (0.041 MPa) since the vapor pressure of hexene-2 is 22.7
psia (0.157 MPa) at 84°C. A lighter hydrocarbon such as
isopentane would require a higher partial pressure of
about 17 psia (0.117 MPa) to achieve a similar reduction
in fines.
10

Example 5

The following example pertains to commercial
production of an ethylene copolymer with hexene-1. This
example was conducted in a commercial reactor as
15   illustrated in Fig. 1. Key elements in the reactor loop
are the reactor vessel 1, heat exchangers 2 and 4,
compressor 3, fines, cyclone 6, and fines return
injector 7. A gas distributor plate 8 is provided near
the bottom of the reactor. An enlarged disengaging zone
20   5 is provided near the top of the vessel for reducing
the entranement of solids in the exiting gas. Various
schemes are used for replenishing the ethylene,
comonomer, hydrogen, and inerts in the main gas recycle
stream. These are depicted in Fig. 1 as a single
25   combined stream 9 for simplicity. Catalyst injection,
in the form of prepolymer, is shown by stream 10, and
polymer powder discharge is shown as stream 11.

The nominal density of the copolymer was controlled
near 0.925 gram per cubic centimeter. The nominal melt
30   index was controlled near 0.9 gram/10 minutes, and the
operating conditions varied in a narrow range. The data
occurred over many month's time, during different
campaigns when this particular type of polyethylene was
produced. The reactor temperature was 78 to 82°C and

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the pressure was about 300 psig (2.07 MPa). Superficial fluidization velocity varied from 1.6 to 2.0 feet per second (49 to 61 cm/sec). Ethylene varied from 24 to 36 mole % of reactor gas composition, with the hexene-1 and
5   hydrogen adjusted to control product density and molecular weight, respectively. The hexene-2 composition in the reactor gas was controlled by adjusting the level of purge, since the hexene-2 is an impurity in the hexene-1 feed. The level of saturated C_6
10 hydrocarbons was adjusted by intentional injection of commercial hexane of the composition described in Example 2. The other particulars of the fluid bed process and the Ziegler catalyst are generally according to Example 2 in U. S. Pat. No. 4,882,400.
15   Fig. 6 shows the reduction in bed fines, as the level of total C_6 was raised over a period of months on 9 successive but separate production campaigns of the same product. As the sum of all C_6 partial pressures was raised above 18 psia (0.124 MPa) from about 12 psia
20 (0.083 MPa), the level of fines, defined as the fraction of the powder less than 125 microns, declined from about 1.6% to about 0.8%.

        The commercial unit sifts agglomerates from the powder withdrawn from the reactor using a screen with
25 openings of 7/16 inch square (1.1 cm square). When the fines were reduced, the production of agglomerates from the screener declined from values above 100 pounds per hour (45 kg/hr) on campaign 1 to values below 2 pounds per hour (1 kg/hr) on subsequent campaigns, even though
30 the production rate for the unit was increased over 50%. Normally, agglomerate production is observed to increase at higher production rates because the reactor is being pushed to higher reaction per unit volume per unit time (space-time yield).

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CLAIMS

We claim:

1.   A process for reducing or controlling the fines in
5   a fluid bed polyethylene process comprising: determining
the fraction of polymeric fines present in the fluid bed
reactor and adjusting the chemical composition of the
fluidizing gas mixture; if the reactor of fines are too
high, then adding an amount of $C_3 - C_8$ hydrocarbon to
10   the gas phase of the reactor.

2.   The process according to Claim 1 wherein, if the
fraction of the fines is reduced below the target
fraction of fines, then the amount of inert $C_3 - C_8$
15   hydrocarbon added to the fluid bed reactor is reduced.

3.   The process according to Claim 1 wherein the
fraction of fines, as measured in percent of total fines
below 125 microns in size, is measured and when found to
20   be above 0.5 weight percent, inert $C_3 - C_8$ hydrocarbon
is added to the reactor.

4.   The process according to Claim 1 wherein the
hydrocarbon is an inert $C_4 - C_6$ hydrocarbon.
25

5.   The process according to Claim 1 wherein the
polymer is an ethylene alpha-olefin copolymer wherein
the comonomer is selected from $C_3 - C_8$ alpha-olefins.

30   6.   The process according to Claim 5 wherein the
ethylene copolymer is an ethylene olefin copolymer and
wherein the comonomer is selected from the group
consisting of hexene-1, 4-methylpentene, pentene-1 and
butene-1.

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7.   The process according to Claim 5 wherein said polyethylene is a linear low-density polyethylene.

8.   The process according to Claim 7 wherein the density of the polyethylene produced in the reactor is between .91 and .94 g/cc.

9.   A process for reducing or controlling the fines in a polyethylene fluid bed reactor comprising determining the ratio of the total reactor pressure to the dewpoint pressure of the reactor gas; if the ratio is below 0.4, then adding an amount of inert C_3 -C_8 hydrocarbon to the reactor to increase the said ratio to at least 0.4 or above.

10.   The process according to Claim 9 wherein the inert hydrocarbon is a C_4 - C_6 hydrocarbon.

11.   The process according to Claim 9 wherein the polymer is an ethylene alpha-olefin copolymer wherein the coolefin is selected from C_3 to C_8 alpha-olefins.

12.   The process according to Claim 9 wherein the ratio of the total reactor pressure to the dewpoint pressure of the reactor gas is maintained between 0.4 and 0.99.

13.   The process according to Claim 12 wherein the ratio of the total reactor pressure to the dewpoint pressure of the reactor gas is maintained between 0.5 and 0.95.

14.   The process according to Claim 13 wherein the ratio of the total reactor pressure to the dewpoint pressure of the reactor is maintained between 0.6 and 0.9.

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15.   A process for the production of polyethylene with a
controlled or reduced fraction of powder fines
comprising:

>   (1) introducing into a fluidized bed of a gas phase
5   reactor at least one alpha-olefin, fluidizing gas,
hydrogen, catalyst, and inert $C_3 - C_8$ hydrocarbon
and measuring the ratio of the total reactor
pressure to the dewpoint pressure of the reactor
gas such that if the ratio is below 0.4, inert $C_3 -$
10   C_8 hydrocarbon is introduced into the reactor, and
if the ratio is above 0.99, reducing the amount of
inert $C_3 - C_8$ hydrocarbon introduced into the
reactor;

(2) removing a portion of the alpha-olefin,
15   fluidizing gas, inert $C_3 - C_8$ hydrocarbon, and
polyethylene produced therein; and

(3) reintroducing fluidizing gas, inert $C_3 - C_8$
hydrocarbon, and alpha olefin.

20   16.   A process for reducing the fines in a
polymerization reactor for producing linear low-density
polyethylene comprising determining the fraction of
polymeric fines present in the fluid bed (or the $P/P*$);
if the fines increase, then adding additional reactive
25   olefin comonomer in the $C_3 - C_8$ range to the reactor gas
mixture along with increasing the amount of ethylene and
hydrogen such that the desired product density and
molecular weight are essentially maintained.

30   17.   The process according to Claim 16 wherein said
reactive olefin comonomer includes one or more olefin in
the range of $C_5 - C_6$.

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18.   The process according to Claim 17 wherein said
reactive olefin comonomer is selected from the group
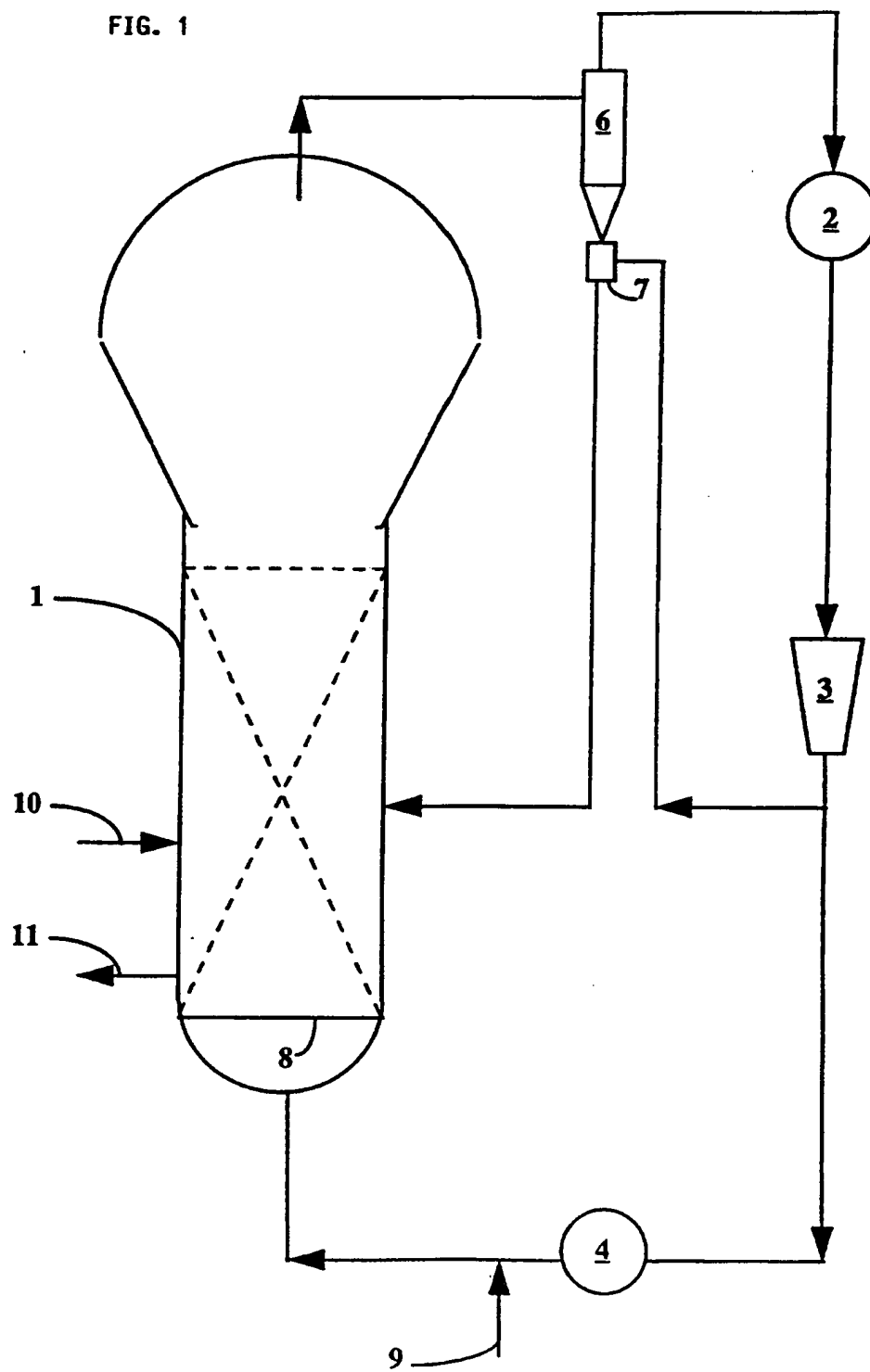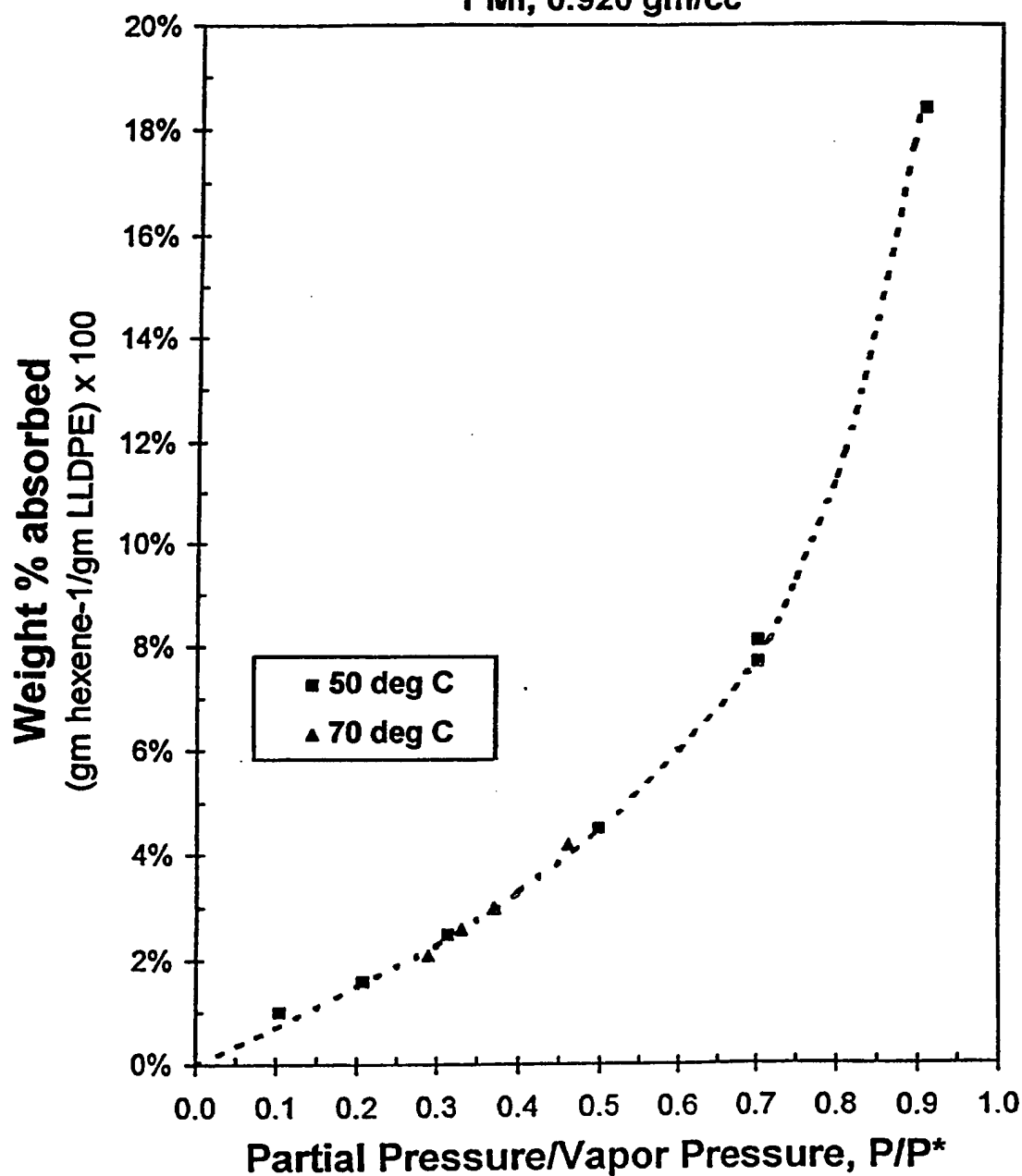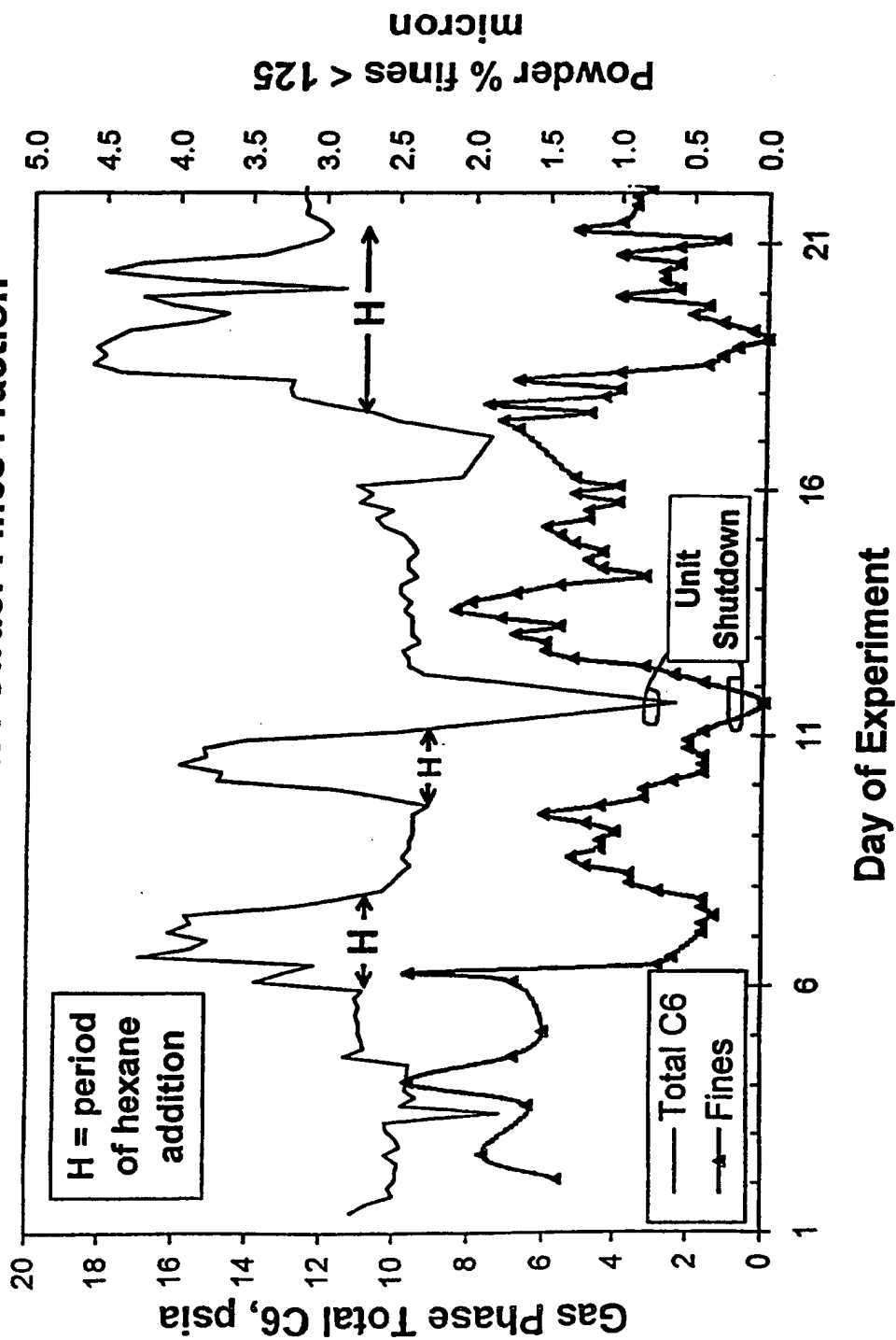consisting of pentene–1, 4–methylpentene–1, and
5   hexene–1.

FIG. 1

FIG. 2

Hexene-1 Absorption in LLDPE
1 MI, 0.920 gm/cc

FIG. 3

Effect of Hexane on Powder Fines Fraction

H = period of hexane addition

Total C6
Fines

Unit Shutdown

Powder % fines < 125 micron

Gas Phase Total C6, psia

Day of Experiment

FIG. 4

Effect of Hexane on Median Particle Size
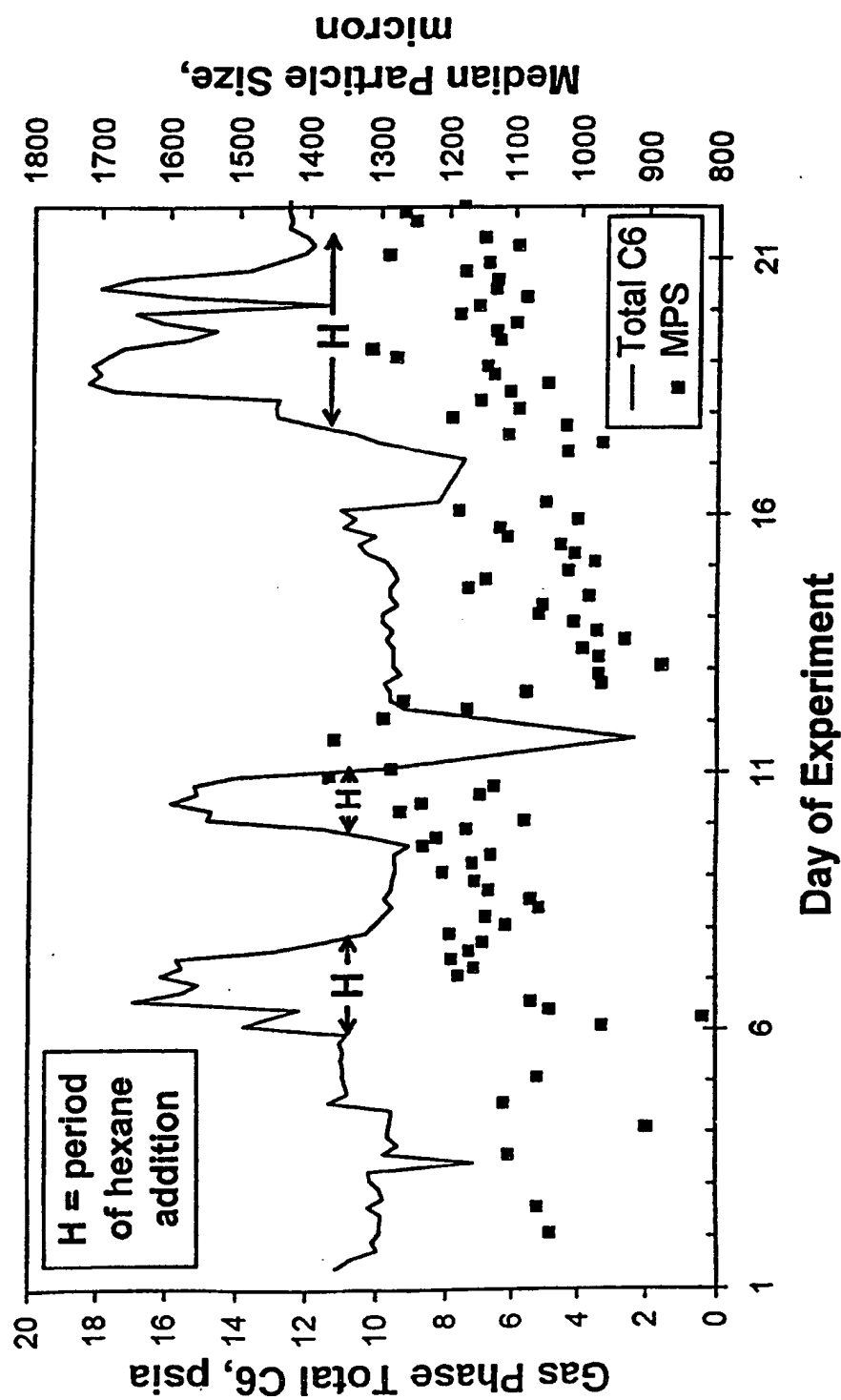
FIG. 5

Dewpoint with Added Hexane

H = period of hexane addition

Total C6

Inlet - Dewpoint
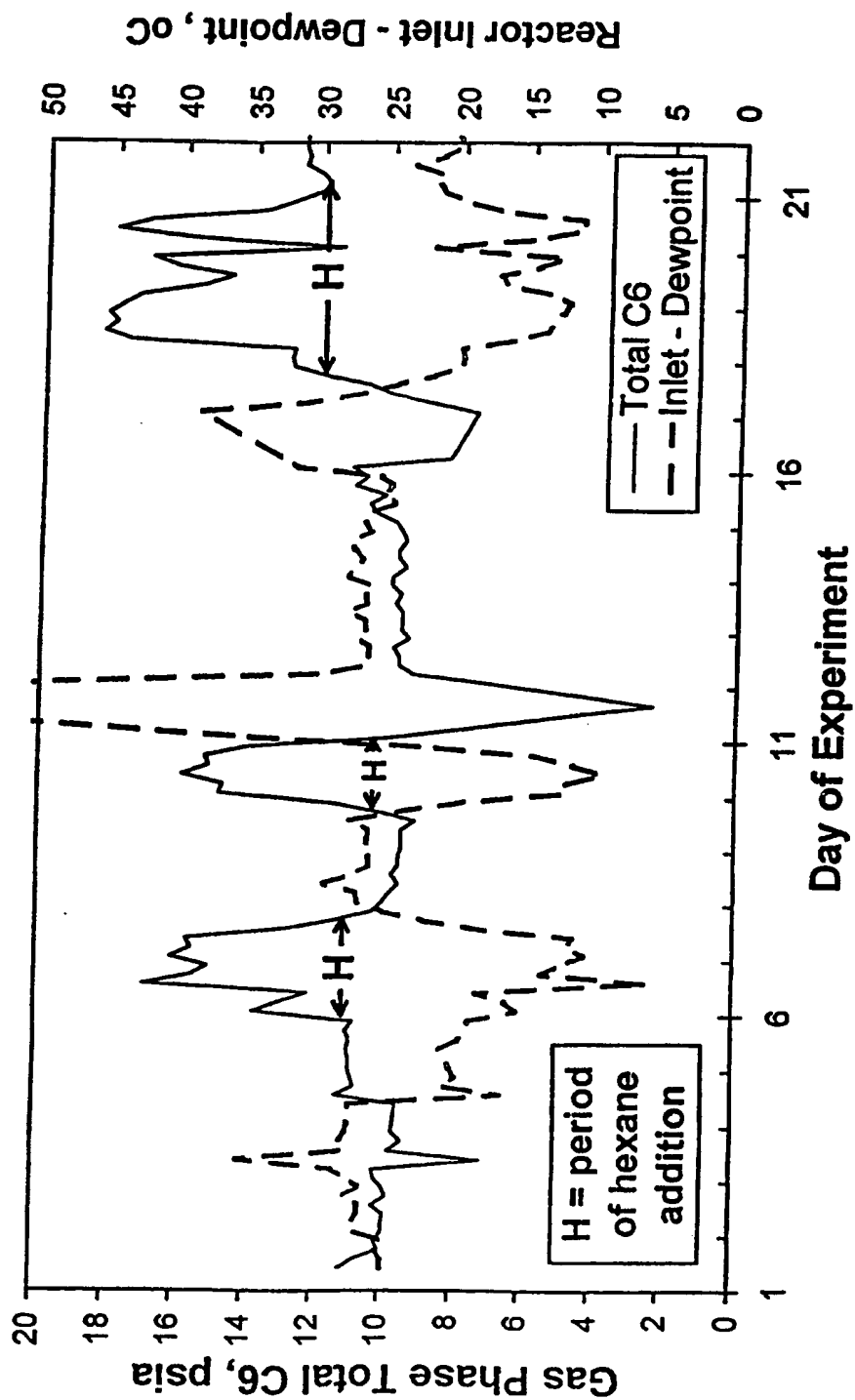
FIG. 6

Fines Level for 0.9 MI, 0.925 gm/cc LLDPE
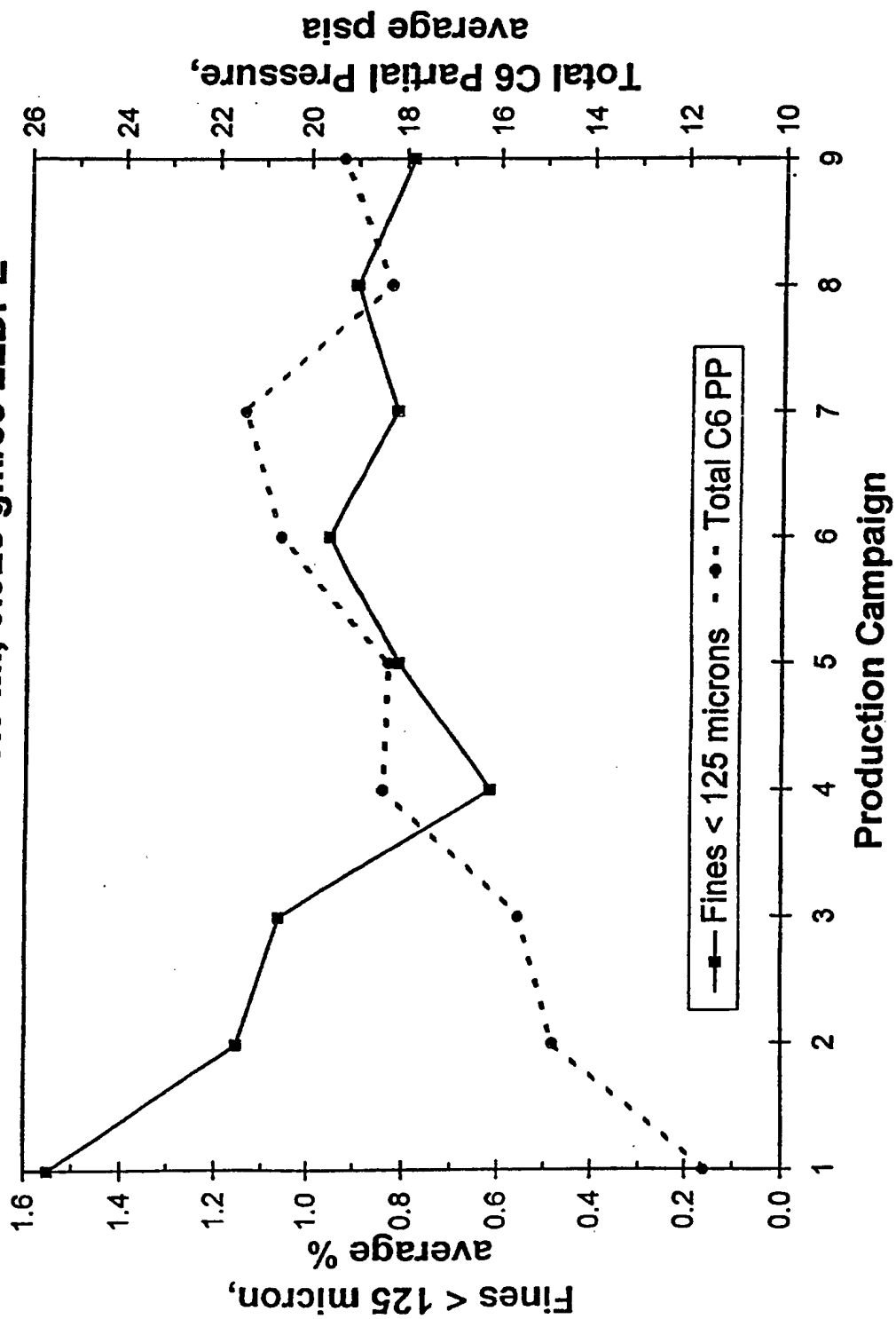
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F2/34   C08F210/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 882 400 A (DUMAIN ANDRE ET AL) 21 November 1989 cited in the application see the whole document ---	1,2,16, 17
A	EP 0 089 691 A (UNION CARBIDE CORP) 28 September 1983 see page 6, line 7 - line 15 see page 13, line 11 - line 23 see page 17, line 11 - line 20; claims ---	1-17
A	EP 0 453 116 A (BP CHEM INT LTD ;BP CHEMICALS SNC (FR)) 23 October 1991 cited in the application see page 5, line 1 - line 3; claims ---	1-17
A	EP 0 571 826 A (BASF AG) 1 December 1993 see page 6, line 31 - line 42; claims ---	1-17

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
14 January 1997	2 7. 01. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Kaumann, E

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 352 749 A (DECHELLIS MARC L ET AL) 4 October 1994 cited in the application see column 5, line 46 - column 7, line 23; claims -----	1-17

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